Statistical and Thermal Physics: Class Exam I

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Name: Taylor Larrechea **Total:** /50

Instructions

- There are 6 questions on 9 pages.
- Show your reasoning and calculations and always justify your answers.

Physical constants and useful formulae

$R = 8.31\,\text{J/mol K}$ $N_A = 6.02 \times 10^{23}\,\text{mol}^{-1}$ $k = 1.38 \times 10^{-23}\,\text{J/K}$ $1\,\text{atm} = 1.01 \times 10^{5}\,\text{Pa}$

Question 1

An ideal gas undergoes a process in which its volume increases by a factor of 4 and its temperature increases by a factor of 3. By what factor is the final pressure related to the initial pressure?

$V_f = 4V_i$ $T_f = 3T_i$

$PV = NkT \rightarrow Nk = \frac{PV}{T}$

$\frac{P_i \cancel{V_i}}{\cancel{T_i}} = \frac{P_f \cdot 4\cancel{V_i}}{3\cancel{T_i}}$ $\therefore$ $\boxed{P_f = \frac{3}{4} P_i}$

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Question 2

Answer either part a) or part b) for full credit for this problem.

a) Determine the isobaric expansion coefficient **and** the isothermal compressibility for an ideal gas.

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad : \quad PV = NkT$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk}{P} \quad \therefore \quad \alpha = \frac{1}{V}\cdot\frac{Nk}{P} = \frac{Nk}{PV} = \frac{\cancel{Nk}}{\cancel{Nk}T}$$

$$\boxed{\alpha = \frac{1}{T}}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{-NkT}{P^2} \quad \therefore \quad \kappa = \frac{-1}{V}\cdot\frac{-NkT}{P^2} = \frac{NkT}{VP^2} = \frac{PV}{P^2\cancel{V}} = \frac{1}{P}$$

$$\boxed{\kappa = \frac{1}{P}}$$

Question 2 continued . . .

b) A monoatomic ideal gas undergoes an adiabatic expansion in which its volume increases by a factor of eight. Determine the work done on the gas in terms of the initial volume and pressure. Note that $\gamma = 5/3$.

$$PV^{\gamma} = \text{Const} \quad , \quad W = -Pdv = -P\int dv = -PV^{\gamma}\int v^{-\gamma} dv$$

$$W = -P_iV_i^{\gamma} \int v^{-\gamma} dv = -P_iV_i^{\gamma}\left(\frac{v^{(1-\gamma)}}{1-\gamma}\right)\Bigg|_{V_i}^{V_F}$$

$$W = \frac{-P_iV_i^{\gamma}}{1-\gamma}\left(V_f^{(1-\gamma)} - V_i^{(1-\gamma)}\right) = \frac{-P_iV_i^{\gamma}}{1-\gamma}\left((8V_i)^{(1-\gamma)} - V_i^{(1-\gamma)}\right)$$

$$W = \frac{-P_iV_i^{\gamma}V_i^{(1-\gamma)}}{1-\gamma}\left(8^{(1-\gamma)} - 1\right) = \frac{3}{2}P_iV_i\left(8^{-2/3} - 1\right) = \frac{3}{2}P_iV_i\left(-\frac{3}{4}\right)$$

$$\boxed{W = -\frac{9}{8}P_iV_i}$$

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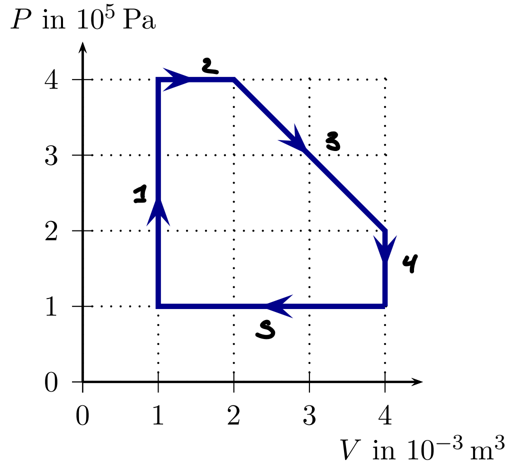
Question 3

A heat engine operates by having a monoatomic ideal gas undergo the process indicated on the PV diagram.



a) Determine the work done by the engine in one cycle.

$W = -P\Delta V = -\text{area under curve}$

$W_1 = W_4 = 0$

$W_2 = -(4.0\times10^5\,\text{Pa})(1.0\times10^{-3}\,\text{m}^3) = -400\,\text{J}$

$W_5 = -(1.0\times10^5\,\text{Pa})(-3.0\times10^{-3}\,\text{m}^3) = 300\,\text{J}$

$W_3 = -(2.0\times10^5\,\text{Pa})(1.0\times10^{-3}\,\text{m}^3) - (2.0\times10^5\,\text{Pa})(2.0\times10^{-3}\,\text{m}^3) = -200\,\text{J} - 400\,\text{J} = -600\,\text{J}$

$W_1 + W_2 + W_3 + W_4 + W_5 = -400\,\text{J} + 300\,\text{J} - 600\,\text{J} = -700\,\text{J}$

$\boxed{W_{net} = -700\,\text{J}}$

b) Determine the heat that enters the gas during the cycle.

$\Delta E = Q + \Delta W \quad \therefore \quad Q = \Delta E - W$

$Q_1 = \Delta E_1 - \cancel{W_1}^{0} \quad \therefore \quad Q_1 = \Delta E_1 = \frac{3}{2}\Delta(PV) = \frac{3}{2}(400\,\text{J} - 100\,\text{J}) = \frac{3}{2}(300\,\text{J}) = 450\,\text{J}$

$Q_2 = \Delta E_2 - W_2 = \frac{3}{2}\Delta(PV) + 400\,\text{J} = \frac{3}{2}(800\,\text{J} - 400\,\text{J}) + 400\,\text{J} = \frac{3}{2}(400\,\text{J}) + 400\,\text{J} = 1000\,\text{J}$

$Q_3 = \Delta E_3 - W_3 = \frac{3}{2}\Delta(PV) + 600\,\text{J} = \frac{3}{2}(800\,\text{J} - 800\,\text{J}) + 600\,\text{J} = \frac{3}{2}(0\,\text{J}) + 600\,\text{J} = 600\,\text{J}$

Question 3 continued . . .

$$Q_4 = \Delta E_4 - \cancel{W_4}^{0} = \frac{3}{2}\Delta(PV) = \frac{3}{2}(400J - 800J) = \frac{3}{2}(-400J) = -600J$$

$$Q_5 = \Delta E_5 - W_5 = \frac{3}{2}\Delta(PV) - 300J = \frac{3}{2}(100J - 400J) - 300J = \frac{3}{2}(-300J) + 300J = -750J$$

$$Q_{net} = 450J + 1000J + \cancel{600J} - \cancel{600J} - 750J = 700J$$

$$\boxed{Q_{net} = 700J}$$

c) Determine the efficiency of the engine.

$$\eta \leq \left|\frac{W_{net}}{Q_+}\right| \leq \left|\frac{-700J}{2050J}\right| \leq 0.34$$

$$\boxed{\eta \leq 0.34}$$

d) Determine expressions for the minimum temperature of the high temperature reservoir and the maximum temperature of the low temperature reservoir needed to run this engine. Determine the optimal efficiency of any engine using these reservoirs.

$$\eta \leq 1 - \frac{T_L}{T_H} : \quad 0.34 \leq 1 - \frac{T_L}{T_H} \quad -0.66 \leq -\frac{T_L}{T_H} \quad \therefore \quad \boxed{\begin{array}{l} T_L \geq 0.66\, T_H \\ T_H \leq \dfrac{T_L}{0.66} \end{array}}$$

$$T_L \approx 12k, \quad T_H \approx 96k$$

$$\eta \leq 1 - \frac{12k}{96k} \leq 1 - \frac{1}{8} \leq \frac{7}{8} \qquad \boxed{\eta \leq \frac{7}{8}}$$

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Question 4

Consider an ideal gas that is thermally isolated from its surroundings. The gas is allowed to expand freely into a region, also isolated thermally from its surroundings, and which was previously a vacuum.

a) Which of the following is true?

   i) The temperature at the end of the expansion is the same as at the beginning.
   ii) The temperature at the end of the expansion is higher than at the beginning.
   iii) The temperature at the end of the expansion is lower than at the beginning.

b) Which of the following is true?

   i) The entropy at the end of the expansion is the same as at the beginning.
   ii) The entropy at the end of the expansion is higher than at the beginning.
   iii) The entropy at the end of the expansion is lower than at the beginning.

Briefly explain your answers.

$\Delta E = \frac{3}{2} Nk\Delta T$: Thermally isolated means $\Delta T = 0$ $\therefore \Delta E = 0$

$S = fNk \ln(T) + Nk\ln(V) + \tilde{h}(N)$

$\Delta S = fNk \cancel{\ln}(T_i) - fNk\cancel{\ln}(T_i) + Nk \ln(V_f/V_i) + \cancel{\tilde{h}(N)} - \cancel{\tilde{h}(N)}$

$\Delta S = Nk \ln(V_f/V_i) \rightarrow \frac{V_f}{V_i} > 1 \therefore \Delta S > 0$

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Question 5

Answer either part a) or part b) for full credit for this problem.

a) Consider a system with a fixed number of particles. Starting with the fundamental thermodynamic identity, show that

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_V .$$

$dE = TdS - PdV$, $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$, $dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial P}\right)_T dV$

$dE = T\left(\frac{\partial S}{\partial T}\right)dT + \left(T\left(\frac{\partial S}{\partial V}\right)_T - P\right)dV$

$\underbrace{\left(\frac{\partial E}{\partial T}\right)_V}_{C_V} dT + \left(\frac{\partial E}{\partial P}\right)_T dV = T\left(\frac{\partial S}{\partial T}\right)dT + \left(T\left(\frac{\partial S}{\partial V}\right)_T - P\right)dV$

$$\boxed{C_V = T\left(\frac{\partial S}{\partial T}\right)dT}$$

Question 5 continued . . .

b) Using the Gibbs free energy, $G = E - TS + PV$, show that

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

$dG = dE - Tds - sdT + Pdv + vdP$, $dE = Tds - Pdv$

$= \cancel{Tds} - \cancel{Pdv} - \cancel{Tds} - sdT + \cancel{Pdv} + vdP$

$dG = vdP - sdT$, $dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$

$\left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT = vdP - sdT \quad \therefore \quad V = \left(\frac{\partial G}{\partial P}\right)_T , \ S = -\left(\frac{\partial G}{\partial T}\right)_P$

$\frac{\partial v}{\partial T} = \frac{\partial^2 G}{\partial T \partial P}$, $\frac{\partial S}{\partial P} = -\frac{\partial^2 G}{\partial P \partial T}$, $\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T} \quad \therefore$

$$\boxed{-\left(\frac{\partial v}{\partial T}\right)_{P,N} = \left(\frac{\partial S}{\partial P}\right)_{T,N}}$$

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Question 6

A particular chemical reaction takes places in contact with a reservoir at temperature of 298 K and a pressure of 1.00 atm. It is determined that for this reaction $\Delta H = -300\,\mathrm{kJ\ mol^{-1}}$ and $\Delta S = -800\,\mathrm{J\ mol^{-1}}$

a) Determine the change in Gibbs free energy, ΔG, for this reaction.

$H = E + PV$, $G = E - TS + PV$, $G = H - TS$ ∴ $\Delta G = \Delta H - T\Delta S$

$\Delta G = -300{,}000\ \mathrm{J/mol} - 298\mathrm{k}(-800\mathrm{J/mol\,K}) =$

$$\boxed{\Delta G = -61{,}600\ \mathrm{J/mol}}$$

b) Can this reaction occur without any non-mechanical work done on the system? For your choice describe either how much non-mechanical work the reaction could produce or how much it would require.

NO W_{nm} on System : $\Delta G \leq W_{nm}$ ⋮ W_{nm} on System : $-\Delta G \leq W_{nm}$

This reaction would produce 61,600 J of non-mechanical work

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